

Spatial Distributions of Heavy Metals in the Water and Sediments of Lake Çıldır, Turkey

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Abstract

In this study, the heavy metal levels were determined for the water and surface sediments of Lake Çıldır. The sediment particle size, organic carbon content, and pH were determined in the lake sediments in addition to the determination of the spatial distribution of heavy metals, as well as the metal enrichment levels for the sediment. The results of the metal analysis obtained using the Inductively Coupled Plasma Mass Spectrometry (ICP-MS) technique indicated that the metal levels in Lake Çıldır and spring waters which feed the lake were identified as Class 1 water quality according to the Turkish Surface Water Quality Regulation limits. Although the Ni and Cr levels found in the sediment were higher than some Sediment Quality Guideline (SQG) limits, the Ni and Cr levels of the core samples representing past periods provided no indication of enrichment for these elements. The spatial distribution of metals in Lake Çıldır was found to be affected by the depth, water inflows, outflows, and a derivation channel that has recently been built.

Keywords: Heavy metals, ICP-MS, Lake Çıldır, metal enrichment, sediment.

Çıldır Gölü (Türkiye) Su ve Sedimentlerinde Ağır Metallerin Alansal Dağılımları

Özet

Bu çalışmada Çıldır Gölünde su ve yüzey sedimentlerindeki ağır metal düzeyleri belirlenmiştir. Göl sedimentlerinde, ağır metallerin yanısıra tane boyu, organik karbon ve pH'nın alansal dağılımları ortaya konulmuş ayrıca sediment için metal zenginleşme düzeyleri tespit edilmiştir. İndüktif Eşleştirilmiş Plazma - Kütle Spektrometri (ICP-MS) tekniği kullanılarak gerçekleştirilen metal analiz sonuçlarına göre Çıldır Gölü ve gölü besleyen kaynak sularındaki metal düzeylerinin Yüzeysel Su Kalitesi Yönetmeliği (Türkiye) limitleri açısından 1. Sınıf su kalitesinde olduğu belirlenmiştir. Sedimentte tespit edilen nikel (Ni) ve krom (Cr) düzeyleri bazı Sediment Kalite Kriterleri (SQG) limitlerinin üzerinde olmasına rağmen geçmiş dönemleri temsil eden sediment karot örneklerine göre bu elementler için bir zenginleşme söz konusu değildir. Çıldır gölünde metallerin alansal dağılımında ise derinlik, su girdi, çıktıkları ile yakın zamanda yapılmış olan derivasyon kanalının etkili olduğu belirlenmiştir.

Anahtar Kelimeler: Ağır metaller, Çıldır Gölü, ICP-MS, metal zenginleşmesi, sediment.

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INTRODUCTION

Lakes interact with three major components of a hydrological system, including atmospheric, surface, and groundwater (O'Sullivan and Reynolds 2003a). Chemical properties of lake waters are closely related to water inflows, outflows, and evaporation (Varekampa et al. 2000). Most pollutants are conveyed by rivers to the lakes and seas, but certain pollutants are conveyed by the atmosphere (O'Sullivan and Reynolds 2003a).

Heavy metals are resistant to degradation under natural conditions so they are the most persistent

pollutants in the ecosystems (Suresh et al. 2012). Heavy metals reach lakes as a result of natural events such as erosion of rocks, volcanic activities, or anthropogenic activities such as mining, smelting, burning fossil fuels, and various industrial processes (Brönmark and Hansson 2005). Due to their low solubility in water, metals often accumulate in the sediment (Suresh et al. 2012).

Lake sediments are an important components of the ecosystems because they provide nutrients for living organisms (Suresh et al. 2012). The composition of lake sediments is affected by the

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geomorphology of the base and drainage basin, whereas, the chemical composition of the sediment is affected by both the lithogenic activities and the changes in climate and the drainage basin (Yıldız and Yener 2010). For this reason, one of the priority issues is to determine the contaminant levels in the sediment.

Volcanic lakes are significantly influenced by acid rain and metal pollution because they have low conductivity and a weak buffer capacity (O'Sullivan and Reynolds 2003b). Lake Çıldır, which is a volcanic set lake located within the provincial borders of Ardahan-Kars, is the largest freshwater lake of the Eastern Anatolia Region of Turkey. The aim of this study was to characterize the water and sediments of Lake Çıldır, clarify the sediment enrichment levels and identify the spatial distribution of heavy metals.

MATERIAL AND METHODS

Study Area

Lake Çıldır is located at 1959 meters above sea level, covers an area of 124 km², and the length and width of the lake is 18.3 km (north-south) and 16.2 km (east-west) respectively. Depending on the climatic conditions, the lake is usually covered by a layer of ice that is thicker than 60 to 70 cm during the winter. Although the lake has multiple inflows including Gölebakan (Yandere: 0.429 m³/sec), Gölbelen (0.163 m³/sec), Gülyüzü (Büyükçay), Dogruyol, Taşköprü and Lavaşın creeks, along with snow and rain water there is only one outflow, Telek Water (Fig. 1). Until recently, Lake Çıldır has been used for drinking water, but nowadays it is used for irrigation and energy production purposes.

Water and Sediment Sampling

The water and sediment samples were collected from 16 stations from Lake Çıldır (Fig. 1) in September 2011 and July 2013. Positions of sampling points were determined by GPS (Garmin Etrex, Taiwan) and sediment samples were taken using an Ekman grap (Hydrobios, Germany). Sediment core sampling was performed for the purpose of using it as background value during determination of the enrichment factor. The collected sediment samples were placed in plastic bags and taken to the laboratory with an ice cooled container.

Water samples were collected from the surface and bottom of the lake at the same 16 sampling stations using Nansen bottles (Hydrobios,

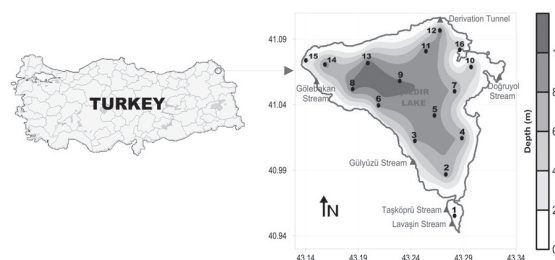


Fig. 1. Sediment and water sampling stations in Lake Çıldır.

Germany). Samples were filtered through 0.45 μm membrane filters before adding ultrapure HNO₃ and taken to the laboratory with an ice cooled container.

In this study aluminium (Al), vanadium (V), chrome (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), molybdenum (Mo), cadmium (Cd), antimony (Sb), mercury (Hg), and lead (Pb) were found in the water samples and Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Cd, Ag, and Pb were detected in the sediments.

Particle Size Analysis of Sediments

Particle size analysis of sediments was performed according to the method of Udden (1914) and Wentworth (1922) using sieves with a pore diameter of 63 μm, 125 μm, 250 μm, 500 μm, 1 mm, and 2 mm (Retsch, Germany).

Analysis of Heavy Metals in the Water and Sediment

Sediments having a particle size below 63 microns were dried at 45°C. They were digested by using 6 mL of HNO₃, 1 mL of HClO₄, and 1 mL of H₂O₂ and a microwave digestion system and then completed to a volume of 25 mL with deionized water (Milestone 2011).

The heavy metal analysis was performed directly on the water samples and diluted sediment samples with a ICP-MS (Varian 820, Melbourne, Australia). Scandium (Sc), Indium (In), and Yttrium (Y) were used as the internal standards.

Other Chemical Analyses of the Sediment Samples

A total organic carbon analysis (TOC) was performed on the sediment samples sieved through a pore diameter of 500 μm using the modified method of Walkley and Black, (1934) and the carbonate determination was performed with the sediments sieved through a pore diameter of 2 mm

with the method of Allison and Moodie (1965), the total phosphorus (TP) determination was performed titrimetrically using the method of Bray and Kurtz (1945), and the pH and electrical conductivity (EC) measurements were performed with the method of Kacar (1994).

Enrichment Factor (EF)

The determination of the Enrichment Factor in the sediment was calculated according to the method of Sutherland (2000) by applying Al normalization.

$$\text{Enrichment Factor (EF)} = \frac{[(\text{Me}/\text{Al})_{\text{sample}}]}{[(\text{Me}/\text{Al})_{\text{background}}]}$$

where the $(\text{Me}/\text{Al})_{\text{sample}}$ is the Metal/ Aluminium ratio in the concerned samples and the $(\text{Me}/\text{Al})_{\text{background}}$ is the natural background value of the Metal/Aluminium ratio. The means metal values belonging to the sediment below 30 cm taken from the core samples were used as natural background values.

Sediment quality classes were determined using the EF value. An $\text{EF} < 2$ indicates a deficiency to low enrichment, $2 < \text{EF} < 5$ is moderate enrichment, $5 < \text{EF} < 20$ is a significant enrichment, $20 < \text{EF} < 40$ is a very high enrichment, and $\text{EF} > 40$ is an extremely high enrichment (Sutherland 2000).

RESULTS

The particle size composition of the sediments (a) and spatial distribution of the silt + clay (%) of the material at the stations (b) are given in Figure 2. The sediments of Lake Çıldır consisted of a sandy-muddy character in terms of particle size.

The mean, minimum, and maximum values of all measurements of Lake Çıldır and the spring waters and the Turkish Surface Water Quality Regulation limits (Quality Criteria of Intracratonic Surface Water Resources by their Classification) are given in Table 1 (Anonymous 2012). The mean values of the measurements (EC, pH, TP, CaCO_3 , TOC, and heavy metals) of the surface sediments and some Sediment Quality Guidelines criteria in terms of the heavy metals are given in Table 2.

The phosphorus concentration, which is a very important and limiting element for eutrophication in fresh water ecosystem, ranged from 286.7 to 693.7 mg/kg in the lake sediments. Also pH, electrical conductivity (EC), total organic carbon and carbonate were measured as 7.16 - 7.40, 33.1 - 81.5 ($\mu\text{S}/\text{cm}$), 0.5 - 2.8(%), and 5.60 - 19.4(%) respectively.

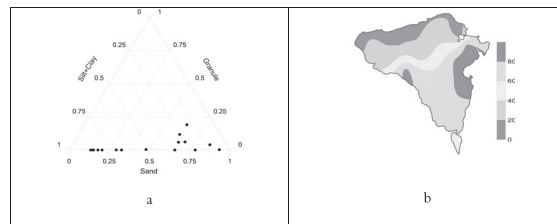


Fig. 2. Particle size composition of sediments (a) and spatial distribution of silt+clay (%) in Lake Çıldır.

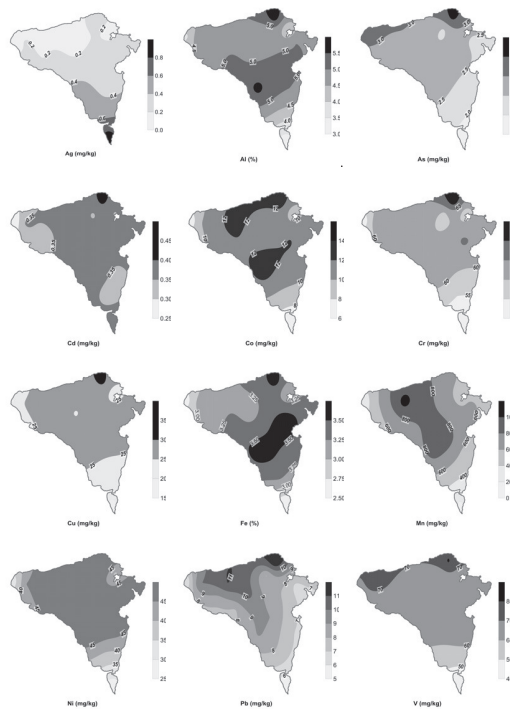


Fig. 3. Spatial distributions of Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and V in Lake Çıldır sediments.

The correlation coefficients among the parameters of the sediments are shown in Table 3. The spatial distribution of metals (Ag, Al, As, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and V) in the surface sediments are given in Figure 3. Zinc (Zn), pH, CaCO_3 , and the TOC spatial distributions are given in Figure 4. The sediment metal concentrations were found to generally increase with depth and decrease with the direction of water flow. The fact that the TP spatial distribution in sediment was in line with the metals can be explained by the precipitation of metals with phosphates. The results of the factor loadings with a varimax rotation, the eigenvalues, and communalities are listed in Table 4.

Table 1. Water quality data of Lake Çıldır and streams water during of September (2011) and July (2013).

| Parameter | Unit | Lake Water | | | Streams Water | | | Water Quality Class* | | | | | |
|-------------|--------|------------|--------------|-------|---------------|---|--------------|----------------------|-------|---------|---------|----------|-----------|
| | | N | Mean±Std.Dev | Min | Max | N | Mean±Std.Dev | Min | Max | 1 | 2 | 3 | 4 |
| Temperature | (°C) | 25 | 17.5±2.5 | 15.2 | 22.7 | 7 | 20.1±5.7 | 11.5 | 26.6 | | | | |
| pH | | 25 | 8.2±0.2 | 7.8 | 8.4 | 7 | 7.9±0.3 | 7.5 | 8.4 | 6.5-8.5 | 6.5-8.5 | 6.0-9.0 | <6.0-9.0> |
| DO | (mg/L) | 25 | 6.7±1.1 | 5.0 | 8.1 | 7 | 7.3±1.7 | 5.0 | 10.2 | > 8 | 6-8 | 3-6 | < 3 |
| Al | (µg/L) | 17 | 1812±151 | 1423 | 2000 | 2 | 33.1±13.2 | 23.8 | 42.4 | | | | |
| V | (µg/L) | 8 | 3.3±0.2 | 3.1 | 3.8 | 5 | 1.9±0.9 | 1.3 | 3.6 | | | | |
| Cr | (µg/L) | 25 | 1.3±1.1 | <0.10 | 2.50 | 7 | <0.10 | <0.10 | 0.29 | | | | |
| Mn | (µg/L) | 25 | 3.6±0.9 | 1.6 | 4.7 | 7 | 2.2±2.6 | <0.10 | 7.1 | | | | |
| Fe | (µg/L) | 17 | 855±66 | 686 | 934 | 2 | 159±120 | 74 | 244 | | | | |
| Co | (µg/L) | 25 | 0.19±0.07 | 0.09 | 0.26 | 7 | 0.11±0.09 | 0.02 | 0.29 | | | | |
| Ni | (µg/L) | 25 | 1.82±0.63 | 0.86 | 3.44 | 7 | 0.61±0.24 | 0.37 | 0.96 | ≤20 | 20-50 | 50-200 | > 200 |
| Cu | (µg/L) | 25 | 2.07±0.81 | 0.48 | 3.50 | 7 | 0.98±0.91 | 0.26 | 2.36 | ≤20 | 20-50 | 50-200 | > 200 |
| Zn | (µg/L) | 25 | 16.8±11.1 | 6.42 | 42.53 | 7 | 29.0±15.2 | 5.9 | 46.3 | ≤200 | 200-500 | 500-2000 | > 2000 |
| As | (µg/L) | 25 | 1.6±0.23 | 1.16 | 1.82 | 7 | 0.85±1.08 | 0.16 | 3.25 | | | | |
| Mo | (µg/L) | 25 | 0.67±0.2 | 0.35 | 0.82 | 7 | - | <0.10 | <0.10 | | | | |
| Cd | (µg/L) | 25 | - | <0.10 | <0.10 | 7 | 0.24±0.14 | 0.11 | 0.48 | ≤ 2 | 2-5 | 5-7 | > 7 |
| Sb | (µg/L) | 25 | - | <0.10 | 0.12 | 7 | - | <0.10 | <0.10 | | | | |
| Hg | (µg/L) | 17 | 0.014 | 0.010 | 0.020 | 7 | - | <0.10 | <0.10 | < 0.1 | 0.1-0.5 | 0.5-2 | > 2 |
| Pb | (µg/L) | 25 | 0.29±0.09 | 0.11 | 0.58 | 7 | - | <0.10 | <0.10 | ≤10 | 10-20 | 20-50 | > 50 |

* Turkish Surface Water Quality Regulation limits (Quality Criteria of Intracratonic Surface Water Resources by their Classification).

Table 2. EC, pH, TP, CaCO₃, TOC and heavy metals concentrations of Lake Çıldır sediments and certain Sediment Quality Guidelines Criterias.

| Parameter | Unit | N | Mean± Std.Dev. | Min | Max | TEL | MET | CBTEL | PEL | TET | CBPEL |
|-------------------|---------|----|----------------|------|------|------|-----|-------|------|-----|-------|
| EC | (mS/cm) | 9 | 51.1±14.0 | 33.1 | 81.5 | | | | | | |
| pH | | 16 | 7.28±0.07 | 7.16 | 7.40 | | | | | | |
| TP | (ppm) | 9 | 420±116 | 287 | 694 | | | | | | |
| CaCO ₃ | (%) | 16 | 12.0±3.9 | 5.6 | 19.4 | | | | | | |
| TOC | (%) | 16 | 2.2±0.6 | 0.5 | 2.8 | | | | | | |
| Al | (%) | 16 | 4.8±0.7 | 3.3 | 5.9 | | | | | | |
| Fe | (%) | 16 | 3.3±0.3 | 2.5 | 3.7 | | | | | | |
| V | (mg/kg) | 16 | 65.1±8.3 | 41.2 | 80.6 | | | | | | |
| Cr | (mg/kg) | 16 | 60.9±5.7 | 50.5 | 74.1 | 37.3 | 55 | 43.4 | 90 | 100 | 111 |
| Mn | (mg/kg) | 16 | 645±230 | 192 | 1067 | | | | | | |
| Co | (mg/kg) | 16 | 10.8±2.0 | 6.4 | 13.5 | | | | | | |
| Ni | (mg/kg) | 16 | 45.1±7.2 | 28.3 | 56.4 | 18 | 35 | 22.7 | 36 | 61 | 48.6 |
| Cu | (mg/kg) | 16 | 25.6±3.4 | 19.8 | 31.6 | 35.7 | 28 | 31.6 | 197 | 86 | 149 |
| Zn | (mg/kg) | 16 | 63.1±9.2 | 38.7 | 78.1 | 123 | 150 | 121 | 315 | 540 | 459 |
| As | (mg/kg) | 16 | 2.7±0.4 | 1.9 | 3.7 | 5.9 | 7 | 9.79 | 17 | 17 | 33.0 |
| Ag | (mg/kg) | 16 | 0.30±0.18 | 0.13 | 0.85 | | | | | | |
| Cd | (mg/kg) | 16 | 0.36±0.04 | 0.26 | 0.41 | | | | | | |
| Pb | (mg/kg) | 16 | 12.7±2.6 | 6.7 | 16.6 | 35 | 42 | 35.8 | 91.3 | 170 | 128 |

TEL: Threshold Effect Level
TET: Toxic Effect Threshold

MET: Minimal Effect Threshold
CBTEL: Consensus-Based TEC

PEL: Probable Effect Level
CBPEL: Consensus- Based PEC

DISCUSSION

The results of the measurements for Lake Çıldır and the spring waters feeding the lake were compared with the trace element limits in the Surface Water Quality Regulation and the water was found to have a class 1 water quality in terms of the trace elements (Ni, Cu, Zn, Cd, Hg, and Pb) reported in the regulation. A statistical difference of

was determined between the lake and water resources feeding the lake in terms of temperature, DO, EC, Al, Cr, Mn, Co, Ni, As, Mo, Ag, Cd, Sb, and Pb concentrations $p < 0.05$. However, the difference in pH, Cu, Zn, and Se concentrations were not significant ($p > 0.05$). Temperature, EC, Al, Mn, Co, Ni, As, Mo, Ag, Sb, and Pb concentrations measured at the lake water stations were higher and

Table 3. Correlation matrix of surface sediments of Lake Çıldır .

| | Depth | pH | EC | CaCO ₃ | TOC | Al | Fe | V | Cr | Mn | Co | Ni | Cu | Zn | As | Ag | Cd | Pb | Granule | Sand | Silt+Clay | |
|-------------------|-------|-------|-------|-------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|-------|-----------|--|
| Depth | 1.00 | | | | | | | | | | | | | | | | | | | | | |
| pH | 0.49 | 1.00 | | | | | | | | | | | | | | | | | | | | |
| EC | -0.78 | -0.51 | 1.00 | | | | | | | | | | | | | | | | | | | |
| CaCO ₃ | 0.42 | 0.59 | -0.42 | 1.00 | | | | | | | | | | | | | | | | | | |
| TOC | -0.07 | -0.35 | 0.41 | 0.04 | 1.00 | | | | | | | | | | | | | | | | | |
| Al | 0.76 | 0.21 | -0.70 | 0.29 | 0.28 | 1.00 | | | | | | | | | | | | | | | | |
| Fe | 0.70 | 0.14 | -0.77 | 0.10 | 0.13 | 0.93 | 1.00 | | | | | | | | | | | | | | | |
| V | 0.88 | 0.41 | -0.65 | 0.50 | 0.33 | 0.87 | 0.79 | 1.00 | | | | | | | | | | | | | | |
| Cr | 0.70 | 0.46 | -0.52 | 0.24 | 0.37 | 0.85 | 0.78 | 0.88 | 1.00 | | | | | | | | | | | | | |
| Mn | 0.74 | 0.41 | -0.73 | 0.37 | 0.06 | 0.92 | 0.80 | 0.77 | 0.80 | 1.00 | | | | | | | | | | | | |
| Co | 0.81 | 0.31 | -0.69 | 0.31 | 0.27 | 0.98 | 0.90 | 0.91 | 0.91 | 0.93 | 1.00 | | | | | | | | | | | |
| Ni | 0.80 | 0.35 | -0.68 | 0.39 | 0.32 | 0.97 | 0.88 | 0.95 | 0.92 | 0.91 | 0.99 | 1.00 | | | | | | | | | | |
| Cu | 0.59 | 0.31 | -0.54 | 0.37 | 0.43 | 0.90 | 0.78 | 0.83 | 0.90 | 0.88 | 0.93 | 0.94 | 1.00 | | | | | | | | | |
| Zn | 0.74 | 0.43 | -0.68 | 0.45 | 0.31 | 0.94 | 0.85 | 0.91 | 0.93 | 0.90 | 0.95 | 0.97 | 0.93 | 1.00 | | | | | | | | |
| As | 0.67 | 0.46 | -0.68 | 0.21 | 0.03 | 0.83 | 0.76 | 0.72 | 0.84 | 0.90 | 0.89 | 0.85 | 0.88 | 0.81 | 1.00 | | | | | | | |
| Ag | -0.89 | -0.58 | 0.72 | -0.57 | -0.15 | -0.76 | -0.72 | -0.96 | -0.82 | -0.70 | -0.81 | -0.86 | -0.71 | -0.85 | -0.64 | 1.00 | | | | | | |
| Cd | -0.40 | -0.10 | 0.07 | -0.06 | 0.30 | 0.22 | 0.18 | -0.11 | 0.20 | 0.25 | 0.16 | 0.15 | 0.40 | 0.25 | 0.28 | 0.24 | 1.00 | | | | | |
| Pb | 0.75 | 0.36 | -0.79 | 0.40 | 0.11 | 0.95 | 0.87 | 0.82 | 0.82 | 0.98 | 0.95 | 0.95 | 0.91 | 0.93 | 0.88 | -0.76 | 0.25 | 1.00 | | | | |
| Granule | 0.43 | 0.56 | 0.03 | 0.22 | -0.15 | -0.09 | -0.26 | 0.22 | 0.17 | 0.07 | 0.05 | 0.06 | -0.05 | 0.01 | 0.11 | -0.31 | -0.64 | -0.05 | 1.00 | | | |
| Sand | -0.05 | 0.33 | 0.28 | 0.01 | -0.43 | -0.53 | -0.65 | -0.34 | -0.33 | -0.24 | -0.41 | -0.42 | -0.44 | -0.45 | -0.22 | 0.21 | -0.52 | -0.38 | 0.81 | 1.00 | | |
| Silt+Clay | 0.00 | -0.36 | -0.26 | -0.03 | 0.41 | 0.49 | 0.62 | 0.29 | 0.29 | 0.21 | 0.37 | 0.38 | 0.41 | 0.42 | 0.19 | -0.16 | 0.54 | 0.36 | -0.84 | -1.00 | 1.00 | |

Table 4. Varimax rotated component loadings of factors and variance explained of Lake Çıldır sediments.

| Parameter | Factor 1 | Factor 2 | Factor 3 | Factor 4 |
|-----------------------|-----------|-----------|-----------|-----------|
| Depth (m) | 0.614283 | -0.213201 | 0.612447 | 0.025749 |
| pH | 0.108668 | -0.026196 | 0.825371 | -0.079717 |
| CaCO ₃ (%) | 0.348639 | -0.454570 | 0.181245 | 0.643034 |
| Organic C (%) | 0.359414 | 0.689106 | 0.078653 | 0.485015 |
| Al (%) | 0.958878 | 0.173572 | 0.017380 | 0.150140 |
| Fe (%) | 0.872471 | 0.392768 | 0.020534 | 0.071765 |
| V (mg/kg) | 0.817310 | -0.507253 | 0.009157 | -0.134715 |
| Cr (mg/kg) | 0.870304 | -0.118773 | 0.066581 | 0.373599 |
| Mn (mg/kg) | 0.665626 | 0.145611 | 0.656105 | 0.158700 |
| Co (mg/kg) | 0.899768 | 0.149171 | 0.321657 | 0.228151 |
| Ni (mg/kg) | 0.936737 | 0.088757 | 0.235718 | 0.227843 |
| Cu (mg/kg) | 0.905739 | 0.134848 | 0.095450 | 0.314129 |
| Zn (mg/kg) | 0.974421 | -0.045890 | 0.046474 | 0.065652 |
| As (mg/kg) | 0.603083 | -0.707269 | -0.106521 | 0.048601 |
| Ag (mg/kg) | -0.488806 | 0.613073 | -0.345963 | 0.357799 |
| Cd (mg/kg) | 0.385855 | 0.325983 | 0.007124 | 0.814735 |
| Pb (mg/kg) | 0.940791 | 0.084437 | 0.169132 | 0.157120 |
| Granule | -0.069840 | -0.346379 | 0.779577 | 0.201097 |
| Sand | -0.251562 | -0.922839 | 0.131466 | 0.001949 |
| Silt+Clay | 0.243770 | 0.910597 | -0.262409 | -0.038318 |
| Expl.Var | 9.410129 | 4.045351 | 2.554952 | 1.934079 |
| Prp.Totl | 0.470506 | 0.202268 | 0.127748 | 0.096704 |
| Eigenvalues | 10.38 | 4.42 | 1.84 | 1.29 |
| % Variance | 51.9 | 22.1 | 9.2 | 6.5 |

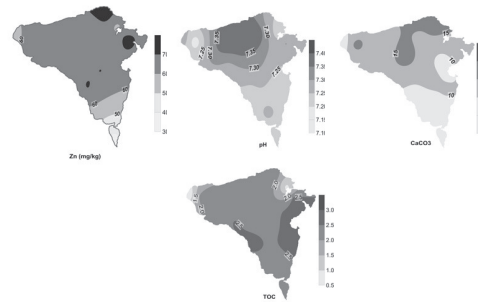


Fig. 4. Spatial distributions of Zn, pH, CaCO₃ (%) and TOC (%) in Lake Çıldır sediments.

Table 5. Comparing of the metal concentrations of Lake Çıldır sediment with some natural and Dam Lake sediments.

| Sediment Sampling Location | Metals (mg/kg) | | | | | | | |
|----------------------------|----------------|---------|---------|----------|----------|-----------|---------|----------|
| | Cr | Mn | Co | Ni | Cu | Zn | As | Pb |
| Çıldır Lake (This study) | 51,1±3,1 | 554±185 | 9,6±1,5 | 37,6±5,5 | 21,8±2,3 | 87,6±16,1 | 3,0±0,6 | 12,9±2,3 |
| Kovada Lake | 17,59 | 165,96 | - | 25,93 | 13,77 | 23,14 | - | 4,42 |
| Tokat Lakes | - | 232 | - | 55,4 | 8,2 | 38,9 | - | 7 |
| Van Lake | 110-420 | - | - | - | 70-760 | - | - | 5-62,82 |
| Hazar Lake | 17-79 | 85-625 | 24-48 | 38-130 | 10-64 | 46-210 | - | <DL |
| Beyler Dam | 19,41 | 346,14 | - | 13,21 | 17,47 | 39,68 | - | 5,62 |
| Seyhan Dam | 118,995 | 803,63 | - | - | 19,8 | 39,09 | - | - |
| Anatürk Dam | - | 73,6 | - | - | 14,57 | 60,79 | - | - |
| Ayşar Dam | 14,48 | - | - | 29,99 | 29,98 | - | - | 2,44 |
| Kıralközü Dam | 22,06 | - | - | 15,75 | 2,83 | 5,02 | 2,39 | 2,56 |
| Batman Dam | 16,5 | - | - | 15,96 | nd | 4,09 | 0,71 | 4,09 |

the dissolved oxygen (DO), Cr, and Cd concentrations were lower than those of the spring waters. The Ni concentrations in the deep waters of Lake Çıldır were higher while the DO concentrations were lower than the surface waters. The Ni and DO differences between the deep and surface water were statistically significant at the level of $p < 0.05$. In terms of the minimum DO values

measured in the waters of the lake as well as some spring waters were of Class 3 water quality during the summer.

When the particle size distributions of Lake Çıldır sediments were examined, it was seen that the large particle size of the sediments in stations 1 and 2 were similar those found in the stations at the

outflow and inflow regions of the lake.

When the correlation tables for Lake Çıldır surface sediments were examined, a high degree of positive correlations between all metals, except for Ag and Cd were remarkable. Ag has a negative correlation with all metals. Although there was a high positive correlation between metals and depth, no significant correlation was identified with the pH, TOC, and carbonate.

There are many sediment quality guidelines approaches used to determine critical levels of pollutant in sediments for freshwater ecosystems (MacDonald et al. 2000). It was determined that the average Cr values in sediments were above the Threshold Effect Level (TEL) and Consensus-Based Sediment Quality Guideline (CBSQG) criteria and the average Ni values were above the TEL, the Minimal Effect Threshold (MET), and CBSQG, as well as the Probable Effect Level (PEL) criteria. It was observed that mean values of the other metals were below the critical values designated for ecological risk. The Ni concentrations detected in the sediment were above the other SQG's critical levels, other than Toxic Effect Threshold (TET) and CBSQG criteria. The Ni concentrations in the inflow waters of Lake Çıldır were low and the Ni concentrations in the deep waters of the lake were higher than that in the surface waters, suggesting that the Ni element was of lithogenic origin.

It was observed that average metal concentrations in the waters of Lake Çıldır were $Al > Fe > Zn > Mn > V > Cu > Ni > As > Cr > Mo > Pb > Co > Sb > Cd > Hg$ in descending order. The average metal concentrations detected in the sediment were as $Al > Fe > Mn > V > Zn > Cr > Ni > Cu > Pb > Co > As > Cd > Ag$ in descending order.

Baltacı, (2011) studied the accumulation levels of iron (Fe), copper (Cu), zinc (Zn), manganese (Mn), cadmium (Cd), and lead (Pb) metals in the muscle tissues of freshwater mussels, and in the sediments at the bottom of the lake and in the water. The heavy metals concentrations were found as $Mn > Fe > Zn > Pb > Cu > Cd$ in the water and $Fe > Mn > Zn > Pb > Cu > Cd$ in the sediment.

The average metal concentrations in natural lakes and dam sediments in Turkey are given in Table 5. All metal concentrations in our study were higher than Kovada Lake (Kır et al. 2007), Beyler Dam Lake (Fındık and Turan 2012), Atatürk Dam

Lake (Karadede and Ünlü 2000) and Kıralkızı and Batman Dam Lakes (Varol 2013).

Nickel (Ni) concentrations in Çıldır Lake sediments were found lower than in Tokat lakes (Mendil and Uluözlü 2007), copper (Cu) concentrations were lower than Avşar Dam Lake (Öztürk et al. 2009), chromium (Cr) and manganese (Mn) concentrations were lower than Seyhan Dam Lake sediments (Çevik et al. 2009).

Lead (Pb) concentrations determined in this study were higher than all the other lakes sediments except Van Lake. The mean zinc (Zn) concentrations determined in Lake Çıldır sediments were higher than the other lakes sediments except for maximum concentration in Hazar Lake (Ozmen et al. 2004).

Maximum concentrations of chromium, copper and lead measured in sediment core samples taken from the Van Lake, were higher than the values measured in this study (Yıldız and Yener 2010).

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Total organic carbon (TOC) in the lake sediments is closely associated with the productivity of the lake. The TOC concentration can also vary depending on the distance to the shore, particle size, sediment input, and carbonate concentration (O'Sullivan and Reynolds 2003c). The higher TOC values were detected in Lake Çıldır sediments from those areas close to stream inflows.

The maximum carbonate values in the sediment were obtained from the stations close to the derivation channel/tunnel, which can be attributed to the structure of the sediment conveyed to the lake

via the derivation channel/tunnel. Research on the sediment carbonate concentrations may provide the basis for the estimation of the lake efficiency, and atmospheric CO₂ concentration in the past (O'Sullivan and Reynolds 2003c).

When the metal enrichment levels in Lake Çıldır sediments were evaluated, it was determined that the only Mn EF value (2.6) was in station 13 which was at a moderate enrichment level, whereas, the EF values of all the remaining metals were at a deficiency to low enrichment (<2) level. Although, particularly Ni and Cr concentrations in the sediment were higher than some SQG limits, the EF values for these metals was low and this can be considered as another evidence of the fact that these metals are of lithogenic origin.

Lastly, the results show that four eigenvalues

explain 89.72% of the total variance. The first factor explains 51.9% of the total variance and loads heavily on Al, Fe, V, Cr, Mn, Co, Ni, Cu, Zn, and Pb. The second factor has a variance of 22.1% and loads mainly on a fine fraction (silt+clay) of the sediments and organic carbon. The other two factors were minimal which have variances of less than 17%. Considering this we may attribute these four factors 1, 2, 3, and 4 as lithogenic, grain size (fine fraction), redox potential, and anthropogenic/biogenic respectively.

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